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ANALYTICAL QUALITY ASSURANCE FOR TRACE ORGANICS ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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16. ABSTRACT

Analytical Quality Assurance concepts are applied to the qualitative analysis of drinking water supplies for trace organics by liquid-liquid extraction and gas chromatography - mass spectrometry. Some of these concepts are also applicable to other methods of analysis.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Potable water Quality assurance Solvent extraction Gas chromatography Chromatographic analysis Mass spectroscopy Qualitative analysis	Finished water analysis Analytical procedures Reagent blank interpretation Finished water Trace organics Gas chromatography - mass spectrometry	13B

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10

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INTRODUCTION

The importance of analytical quality assurance in trace organic pollutant analysis cannot be overestimated. Data generated in surveys are being used to set standards for drinking water, surface water quality, and effluents. Possible correlations between the presence of organic contaminants in drinking water and human health effects are under widespread study. In the past many carefully conducted measurements were not documented with sufficient data to support their reliability. This caused doubt about the validity of the measurements and concern for the correctness of correlations and proposed standards.

The purpose of this report is to describe the application of analytical quality assurance (AQA) concepts to the qualitative analysis of water samples for trace organics. The concentration, isolation, and identification procedures used in this work were liquid-liquid extraction and gas chromatography — mass spectrometry (GC/MS). However, some of the AQA techniques that are described also have applicability in other methods of trace organic analysis including: the entrainment of volatiles in an inert gas stream followed by trapping and GC/MS (1); and carbon or resin adsorption, extraction, and GC/MS (2).

The data used to illustrate the AQA were obtained from five drinking water samples taken during January and February 1975. The samples were collected from Miami, Florida, Seattle, Washington, Philadelphia, Pennsylvania, Cincinnati, Ohio, and Ottumwa, Iowa. The results of these analyses are a part of a larger survey of drinking water supplies that was conducted by several U.S. Environmental Protection Agency (EPA) laboratories during early 1975. Some EPA facilities applied different methodologies of isolation and concentration of the organic contaminants, but GC/MS was always applied for identification of individual pollutants. The different methodologies are effective with different classes of pollutants, but there is some overlap between classes, which serves as an excellent verification of certain results.

The overall philosophy of the survey was to analyze for all organic compounds present in the samples. This is in sharp contrast to many previous studies where the approach was to "analyze for" specific materials of interest. Within this context, the emphasis of the survey was qualitative, i.e., the identification of individual organic compounds in the water. Precise measurement of concentration was not a goal of the survey. A comprehensive report on the results from all methodologies was prepared (3).

EXPERIMENTAL

Glassware

All laboratory glassware was washed with detergent, rinsed with tap water, rinsed with distilled water, and air dried. It was then heated at 400°C for 1 hour in a muffle furnace. Samples were collected in 1-gallon glass jugs supplied with Teflon cap liners. Sample jugs were washed with detergent, rinsed with tap water, air dried, and heated to 400°C for 15 minutes.

Materials

Anhydrous sodium sulfate (Mallinckrodt Analytical Reagent) was used as received. In one experiment a batch of sodium sulfate was placed in a large soxhlet extractor and extracted with 2 liters of hexane/acetone (1:1 v/v) for 24 hours. The sodium sulfate was dried at 120°C and used in normal sample preparation and in the blanks. No reduction in the number or size of the contaminant peaks was observed. It was concluded that no significant amount of contamination was contributed by the sodium sulfate. Acetone, methylene chloride, and diethyl ether were Burdick & Jackson "distilled in glass" and were used as received.

Instrumentation

Mass spectra were measured with a Finnigan 1015 quadrupole mass spectrometer. The inlet system was a Varian Series 1400 gas chromatograph that was interfaced to the spectrometer by an all-glass jet-type enrichment device and an all-glass transfer line. Control of the quadrupole rod mass set voltages, data acquisition, data

reduction, and data output was accomplished with a System Industries data system that employed a Digital Equipment Corporation PDP-8/E mini-computer and a 1.6-million-word Diablo disk drive. Data were displayed on a Tektronix 4010 cathode ray tube (CRT) or a Houston plotter.

The GC column used in this study was a 6-ft (2 mm ID) coiled glass tube packed with Supelcoport (80/100 mesh) coated with 1.5% OV 17 and 1.95% QF 1. The initial column temperature of 60°C was held for 1.5 minutes, then the temperature was programmed at 8°C per minute to a final temperature of 220 C, which was held for 15 minutes. The total run time was approximately 35 minutes. Conditions that were held constant throughout the analyses were: helium carrier gas at a flow rate of about 30 ml per minute; temperature of the GC injection port at 190 C; the temperatures of the interface and transfer line at 210°C; spectrometer manifold temperature at 100°C; pressure in the MS of 10^{-5} torr; ionizing voltage of 70 eV; a filament current of 500μamp; electron multiplier at 3000 volts; mass range scanned from 33-450 amu at an integration time of 8 msec/amu; and sensitivity at 10^{-5} amps/volt.

SCOPE AND LIMITATION OF THE METHOD

The method used applied to all organic compounds present that are extracted partially or completely into the methylene chloride — diethyl ether solvent. All compounds originally present in water at a concentration of approximately 10 ng per liter (0.01 ppb) or greater that elute from the GC column without decomposition within 35 minutes will be observed. Very volatile compounds, e.g., chloroform, vinyl chloride, etc., will not be observed as they are either lost during extract concentration or masked during solvent elution from the GC. For example, compounds that are observed include the following: aliphatic hydrocarbons — C_6 and larger; aromatic hydrocarbons — benzene derivatives, biphenyls, alkyl benzenes, polynuclears, etc.; pesticides — chlorinated, organophosphorus, some carbamates, phenols of all types; PCB's; plasticicers — phthalates, adipates, and sebacates; and various other types of compounds including sulfur compounds, amines, alcohols, aldehydes, ketones, and some carboxylic acids.

PROCEDURE

1. After measuring the pH of the gallon sample (generally pH = 6-8), 3 liters were transferred to a 6-liter separatory funnel. Fifty milliliters of ethyl ether were added, and the mixture was shaken for 1 minute. The sample was then extracted three times with 75-ml portions of methylene chloride, and the extracts were combined in a 300-ml Erlenmeyer flask. The purpose of the ethyl ether was to improve the extraction efficiency of the more polar compounds like phenols and acids.

2. The combined extract was poured through 2 inches of anhydrous sodium sulfate in a 19-mm ID glass column. The dried extract was collected in a 500-ml Kuderna-Danish (K D) flask fitted with a 10-ml ampul graduated in 0.1-ml increments. As an added precaution, the anhydrous sodium sulfate was prerinsed with 100 ml methylene chloride to remove soluble impurities. For each water sample, a parallel experiment was conducted with all quantities of materials and procedures exactly the same as the sample except that no water or aqueous solution was employed. This reagent blank was initiated in this step by pouring 250 ml of methylene chloride — ethyl ether (4:1 v/v) through 2 inches of anhydrous sodium sulfate in a separate 19-mm ID glass column.

3. After the combined extract or blank had filtered through the sodium sulfate, the sodium sulfate was rinsed with 50 ml of acetone. This was done for two reasons: to rinse any residual sample components from the sodium sulfate, and to introduce a nonchlorinated solvent into the sample for GC/MS injection.

4. The pH of the water layer was then adjusted to 2.0 using concentrated HCl and steps 1, 2, and 3 were repeated. In step 1, it was not necessary to add the ethyl ether a second time.

5. When the second extraction was completed, the pH of the water layer was adjusted to 12.0 using a saturated NaOH solution. Again steps 1, 2, and 3 were repeated ignoring the addition of ethyl ether. The three sample extracts were now contained in three K D flasks: the neutral compounds extracted from a solution of approximately pH 7, the acid compounds extracted from a solution of pH 2, and the basic compounds extracted from a solution of pH 12. The reagent

blank was in a separate K D flask.

6. A Snyder column was fitted to each K D flask, and the extracts were concentrated on a steam bath to approximately 5 ml. After concentration the methylene chloride (bp = 39.8°C) was largely removed and the sample was contained in acetone (bp = 56.1°C). The acetone was used because several microliters of methylene chloride will cause an excessive increase in the pressure in the mass spectrometer and cause automatic shut down of the system. Up to 8 μl of acetone will not cause this undesirable situation as it is removed more efficiently by the enrichment device.

7. The extracts were further concentrated in the ampul in a warm water bath under a stream of clean, dry nitrogen to 100 μl with repeated rinsings of the inside of the ampul.

8. Five-microliter injections were made into the GC/MS, with data acquisition started after a delay of 90 seconds.

RESULTS AND DISCUSSION

Sampling information and results of the water analyses are given in Table I. Table II is a summary of the application of AQA techniques to the analyses reported in Table I.

Most of the concentration values in Table I are estimates that were based on conservative extraction efficiencies and average response factors. These estimates are probably accurate to within a factor of ten. In a few cases authentic samples were available and extraction efficiencies and response factors were determined. This permitted better estimates of concentration, and these results are probably accurate to better than ±50%. In no case was a precise concentration measurement attempted by development of a calibration curve with several standards and careful measurement of integrated instrument signals. High precision measurements were beyond the scope of this survey.

Analytical Quality Assurance

The AQA that applies to qualitative organic trace analysis may be conveniently divided into four categories:

(a) reagent and glassware control;
(b) instrumentation control;
(c) supporting experiments; and
(d) data evaluation.

Reagent and glassware control is required to minimize the introduction of contamination from the materials used in the liquid-liquid extraction procedure. Glassware cleaning procedures have been developed and they are effective. High-quality commercial reagents and solvents are available, but quality is still somewhat variable and usually unpredictable. In solvents that are used for extractions, impurities are amplified by about a factor of 2000 during extract concentration. Clearly, if background contaminants that are introduced from reagents or solvents seriously obscure compounds in the sample, purification of these materials is required.

Instrumentation control is required to ensure that the total operating instrumentation system is calibrated and in proper working order. If a computerized GC/MS system is used to collect data, the computer data system must be included in the performance evaluation. The recommended instrumentation control procedure employs a standard reference compound and a set of reference criteria to evaluate the performance of the overall system (4). This evaluation should be performed on each day the GC/MS system is used to acquire data from samples or reagent blanks. The records from the performance evaluations should be maintained with the sample and reagent blank records as permanent documentation supporting the validity of the data.

The reagent blank is a *supporting experiment* required for all samples. This is true even when contamination from glassware and reagents is well controlled. The reagent blank result is the documentation that proves that good control was exercised, and it defines precisely the level of background that was beyond control.

The reagent blank evaluation may be a straightforward comparison of corresponding peaks and mass spectra in the reagent blank and sample. A more rigorous procedure is required to make objective judgments in situations that are not obvious. An effective technique for comparing blanks and samples employs the extracted ion current profile (EICP) of one or several ions. An EICP is defined as a plot of the change in relative abundance of one or several ions as a function of time (5). The data for this plot are extracted from all the ion abundance measurements made over the mass range observed during the elution of the separated components from the GC. The EICP produces an apparent increase in sensitivity by subtracting from the total ion current profile all the ion abundance data contributed from background, unresolved components, and other irrelevant ions. The EICP

TABLE I. RESULTS OF ANALYSES USING LIQUID-LIQUID EXTRACTION AND GC/MS

Location of sampling	Date collected	Date received	Date extracted	Compounds identified	Approximate concentration* μg/l (ppb)
Miami, Fla. Miami-Dade Water & Sewer Authority	1/20/75	1/29/75	1/31/75	bromoform	0.2
				hexachloroethane	0.07
				di-*n*-octyl adipate	20.
				nicotine	3.
Seattle, Wash. Seattle Water Dept.	1/27/75	2/5/75	2/10/75	none	
Philadelphia, Pa. Philadelphia Water Dept.	2/3/75	2/12/75	2/18/75	1,2-bis (2-chloroethoxy)-ethane	0.03
Cincinnati, Ohio Cincinnati Water Works	2/11/75	2/18/75	2/19/75	dibromochloromethane	0.05
				isophorone	0.02
				trimethyl isocyanurate	0.02
Ottumwa, Iowa Ottumwa Water Works	2/17/75	2/26/75	2/28/75	benzoic acid	15.
				phenylacetic acid	4.

*Concentrations are estimated as accurate to within a factor of ten; with d-*n*-octyl adipate, nicotine, and benzoic acid, authentic samples were available and the concentrations of these are probably accurate to within ±50%.

TABLE II. ANALYTICAL QUALITY ASSURANCE IN THE IDENTIFICATION OF ORGANICS

Compounds identified	In blank EICP	Spectrum* matched	GC† retention time	Extracted in fraction	Molecular ion observed	M+1 ion isotope‡ accuracy		Spectrum checked for consistent major fragments
						Calcd %	Found %	
bromoform	no	NIH	very short	neutral	yes	Br_3 pattern		yes
hexachloroethane	no	NIH	short	neutral	no	Cl_6 pattern§		yes
di-*n*-octyl adipate	no	NIH & standard	matched standard	acid same as standard	no	not applicable		no
nicotine	no	NIH & standard	matched standard	base same as standard	yes	10.8	12	yes
1,2-bis(2-chloro-ethoxy)ethane	no	NIH	not applicable	neutral	no	not applicable		yes
dibromochloro-methane	no	NIH	very short	neutral	yes	Br_2Cl pattern		yes
isophorone	no	NIH	not applicable	neutral	yes	9.7	9.1	yes
trimethyl isocyanurate	no	NIH	not applicable	neutral	yes	6.5	7.2	yes
benzoic acid	no	NIH & standard	matched standard	acid	yes	7.6	7.6	yes
phenylacetic acid	no	NIH	not applicable	acid	yes	8.6	7.3	yes

*The computerized mass spectrum matching system used was developed by the National Institutes of Health (NIH) and EPA.

†Precise measurements of retention times were not made because of the difficulty of reproducing the initial temperature conditions exactly.

‡In non-halogen containing compounds, the M+1 ion abundance is expressed as a percentage of the molecular ion abundance in the calculated and experimental values.

§The Cl_6 pattern was observed in the M-Cl ion.

generator is a standard data reduction program on all modern computerized GC/MS systems. A fast graphics display device is required to facilitate reviewing a large number of EICP plots.

It is emphasized that it is not necessary to have even a tentative identification of a compound to apply this technique to reagent blank evaluation. To conduct an EICP comparison, the mass spectra of all peaks in the sample are examined. One or several ions that are prominent in a spectrum from each peak are selected, and the sample and reagent blank EICP's are generated on the CRT. Comparison of these permits, in most cases, straightforward judgments concerning the presence of compounds in the sample and the reagent blank. In Figure 1 is the EICP for mass 171 from a sample and the corresponding reagent blank. Clearly there is a compound having a mass 171 ion in the sample, but there is no corresponding peak above the noise level in the reagent blank.

If a corresponding peak is observed in the reagent blank and its concentration, as judged from the peak height, is approximately the same as or exceeds the sample concentration, the decision is clear and the compound must not be reported. A far more difficult judgment must be made when the concentration of a component in the sample exceeds its concentration in the reagent blank. The material in the sample could, of course, be a true sample component. Alternatively, it has been observed empirically that compounds in the blank sometimes *merely appear* to be at lower concentrations than the same compounds in the corresponding sample. In Figure 2, total ion current profiles for a sample and a corresponding reagent blank are shown. Careful comparison of the profiles reveals a very similar pattern of peaks and valleys in certain areas (e.g., spectrum numbers 170-190 and 235-245) yet a significantly lower apparent concentration in the reagent blank. There are several possible reasons for this. One rationalization is that impurities in the pure solvent are adsorbed more efficiently onto the drying agent and other surfaces, which creates a purifying effect. With extracts containing some water, the wetting effect of the water precludes efficient adsorption on surfaces and the impurities are carried on in the solvent. Alternatively, certain solvent impurities may be lost more readily from the blank than from the sample extract during the concentration step. This may be caused by the general organic background matrix in the sample extract which acts as a *keeper* for the solvent impurities. Both explanations are reasonable but unproved. In view of the uncertainties, any compound that is observed in the sample should not be reported if it is part of an overall pattern of peaks that is repeated in the blank, although at a lower apparent concentration.

Chemical ionization, field ionization, and high-accuracy mass measurements are GC/MS techniques capable of generating very strong evidence in support of identifications. However, the production of this evidence is restricted because only a relatively few laboratories have developed capabilities with these techniques. High-accuracy mass measurements are further limited by sample size, since some sacrifice in sensitivity is required to achieve the high accuracy.

After a tentative identification is made, by either interpretation or empirical spectrum matching, several other types of supporting experiments become possible. The retention time data from the GC/MS of a pure compound (standard) may be compared with analogous data from the sample component. Similarly the mass spectrum of the standard, obtained under the same conditions that were used for the sample, may be compared with the spectrum of sample component. The standard may be dissolved in water at an appropriate concentration, extracted, and measured. The recovery of this spike in the same fraction that the suspected component appeared in and the observation of the same mass spectrum as the sample component gave is a strong confirmation of the correctness of the identification.

The *evaluation of the data* must weigh the available evidence in terms of its reliability and determine the cost and benefits to be gained by gathering additional information.

Clearly the most convincing evidence for an identification is obtained by examining pure standards that correspond to suspected sample components. However, the existence of this evidence is constrained by the availability of the pure standard and the additional cost and time required to examine it. Because it is not usually possible to predict which compounds will be found, some standards will not be available immediately. There are many very practical limitations imposed on the development and maintenance of a large library of pure authentic standards. Many compounds are obtainable from fine chemical supply houses, but procurement time is variable and may extend to weeks or months. Some compounds are not available from any supplier, frequently because they are by-products or metabolites of industrial processes rather than manufactured products. This same limita-

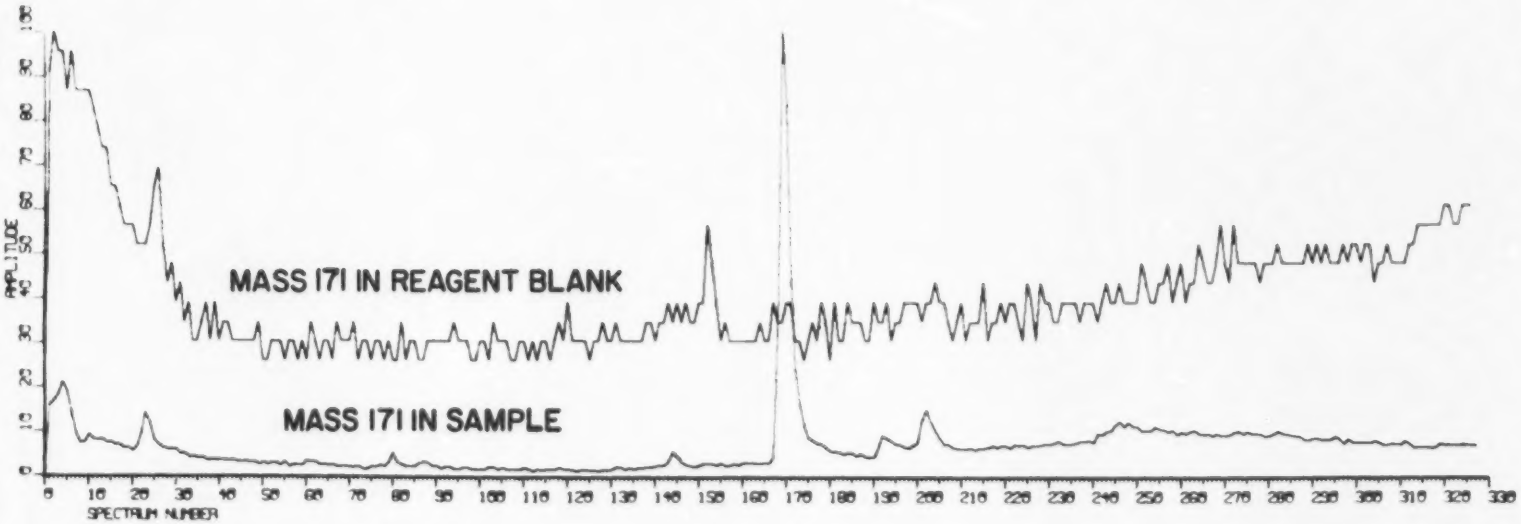

Figure 1. The extracted ion current profiles of mass 171 from the Cincinnati neutral fraction and the corresponding reagent blank.

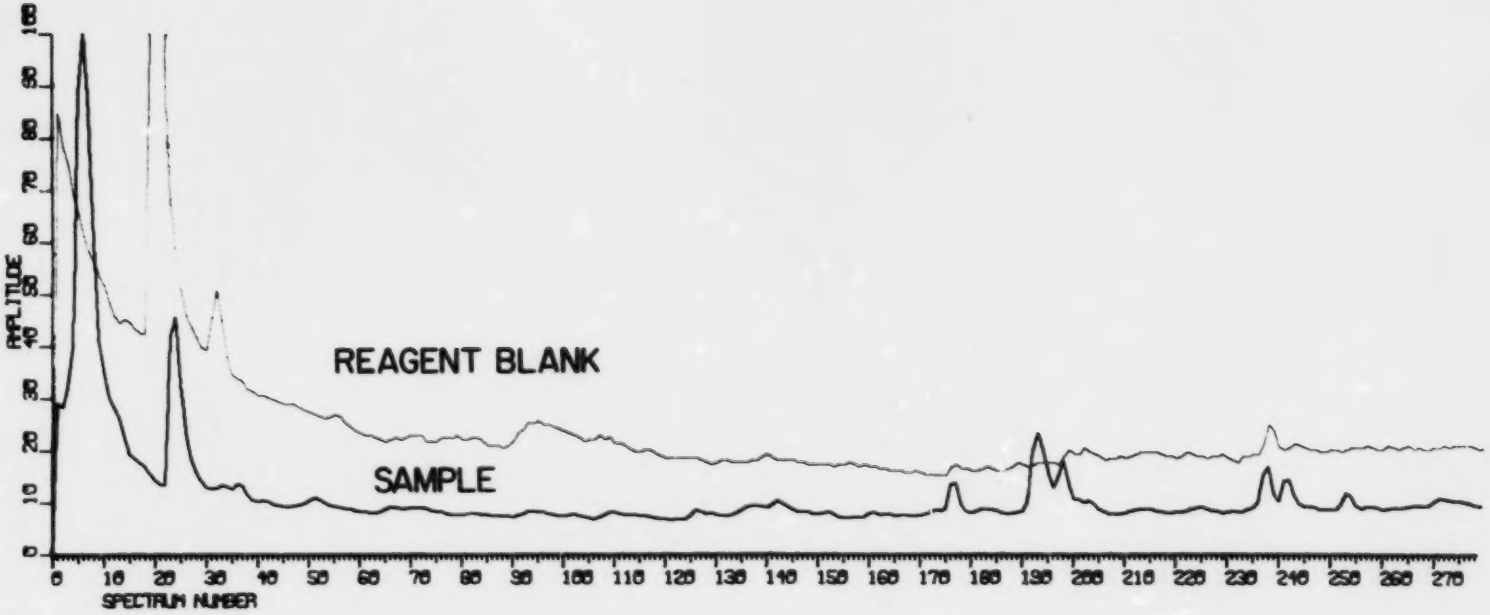

Figure 2. The total ion current profiles for the Philadelphia neutral fraction and the corresponding reagent blank.

tion of standard availability also precludes careful concentration measurements in many cases.

Because of the problem of standard availability, it is worthwhile to determine whether conditions could exist that would lead to reliable identifications without standards. One criteria for a reliable identification that might be used is a quantitative measure of the goodness of match between an experimental mass spectrum and a spectrum from the printed literature or a computer-readable data base. A similarity index (SI), calculated on a scale from zero to one, has been described (6) and used in one computerized mass spectrum matching system (7). Experience with this SI indicates that, in general, a value greater than about four tenths corresponds to the existence of a reasonable match between two mass spectra.

A reasonable match often does imply an identification, but sometimes it does not. It is well known that position isomers and members of homologous series of compounds often give very similar mass spectra. There is another undetermined number of compounds that are simply not uniquely characterized by their mass spectra. Figure 3 is the mass spectrum of an unidentified compound and Figure 4 shows the spectrum of the compound chloropicrin, Cl_3CNO_2. The match is clearly good by inspection, and a SI of 0.453 was calculated. Nevertheless, the compound whose spectrum is in Figure 3 is not chloropicrin as determined by the gas chromatographic behavior of the unknown and pure chloropicrin.

Another problem with identifications based on empirical spectrum matching is that significant differences in ion abundance measurements are sometimes observed when the mass spectrum of a compound is measured on two different spectrometers. Most of these differences are probably caused by non-uniform calibration procedures or a failure to use an ion abundance calibration procedure. In addition, it is well known that different types of inlet systems may have significant effects on relative abundance measurements. With a GC of batch inlet system that is generally operated in the 100-250°C temperature range, temperature-dependent fragmentations are promoted with frequent reductions in the abundances of molecular and other higher mass ions. With a well-designed direct inlet system, these temperature effects may be largely precluded. As a result of these factors, it is quite common for two spectra of the same compound, measured with different inlet systems or spectrometers, to give a rather low SI. A low SI may also be caused by unresolved or partly resolved components which generate mass spectra containing extraneous ion abundance measurements.

It is concluded that the SI must be used with caution. A relatively high SI may be regarded as an indication of a reasonable match, but only as suggestive of the probability of an identification. A relatively low SI cannot be regarded as complete rejection.

Another criterion for reliable identifications when standards are not available is based on an assessment of the quality of the ions in the experimental and reference mass spectra. In the SI calculation (6), molecular ions (M^+), molecular ions having naturally occurring isotopes (typically M+1), and all key fragment ions are weighted the same as many very common fragment ions. However, the M^+, for example, is unique in every mass spectrum and has significance to an identification that far outweighs most other ions. Mass spectra may be categorized according to the quality of the ions observed, and a quality index (QI) can be calculated that is a weighting factor for the SI. Several categories of quality are:

(a) The highest quality spectrum is one in which the molecular ion is observed and the observed distribution of abundances for it and its isotope-containing species is within 10% of the expected distribution. For this spectrum, the QI is 1.0 and the full SI value is retained with considerably enhanced significance.

(b) If a molecular ion is observed but the isotope data are not within 10% of the expected value, lower confidence is assigned by a QI of 0.75.

(c) Failure to observe a molecular ion but observation of key fragments that account for all the atoms of the molecular ion suggests a QI of 0.5. This index may be raised or lowered between 0.4 and 0.6 depending on the observation of consistent isotope data in the key fragment ions.

(d) Finally, the lowest confidence is placed on spectra which do not contain adequate fragment ions to account for all the atoms of the molecular ion. A QI of 0.1 is assigned to these spectra.

It is recognized that position isomers may not be distinguishable under any circumstances, but this is often true even when pure standards are available.

The QI is amenable to additional positive adjustments by 0.1-0.2 QI units if all major fragment ions are scrutinized and found to be reasonable and compatible with the assigned

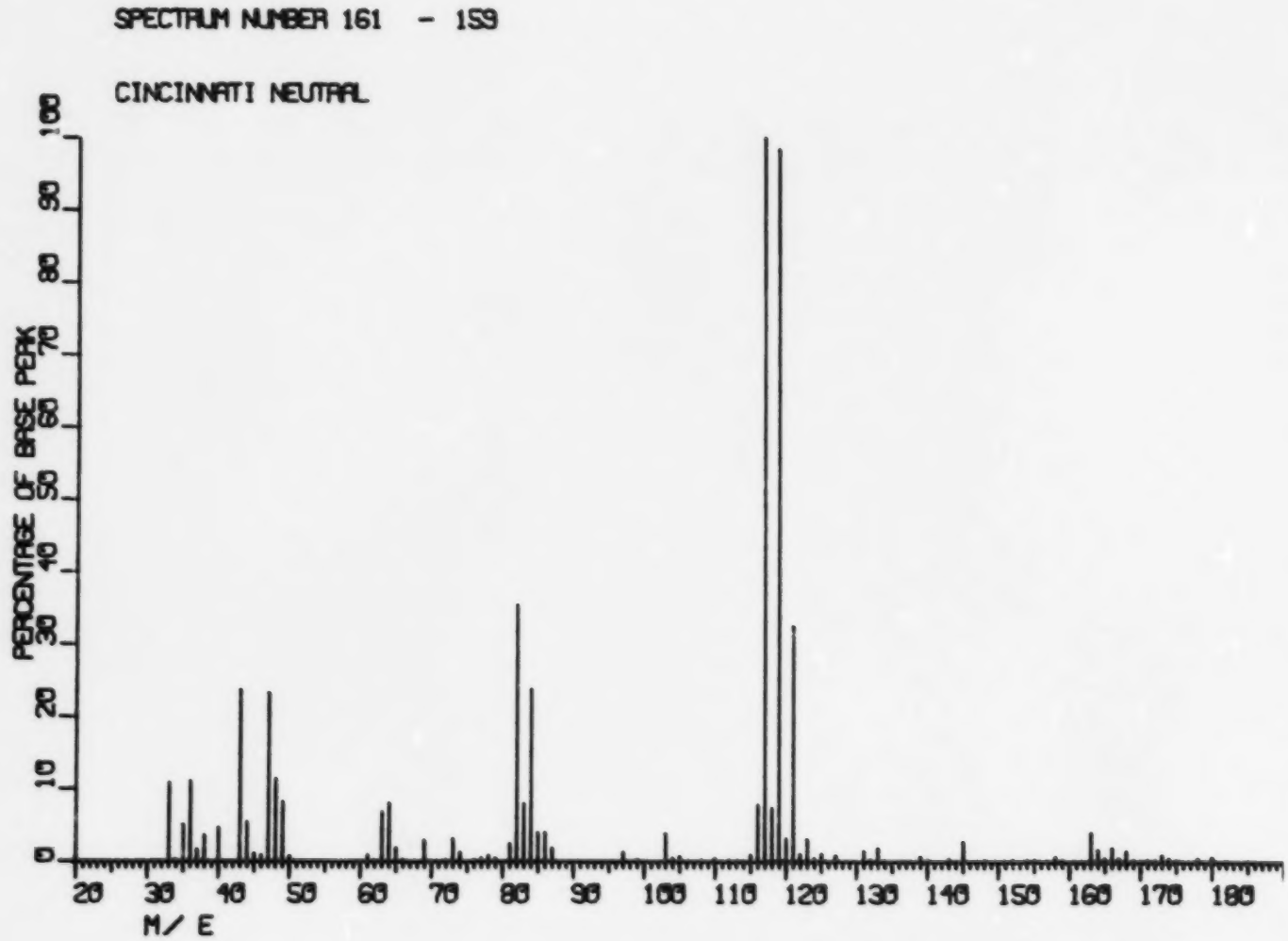

Figure 3. The mass spectrum of a compound found in the Cincinnati neutral fraction.

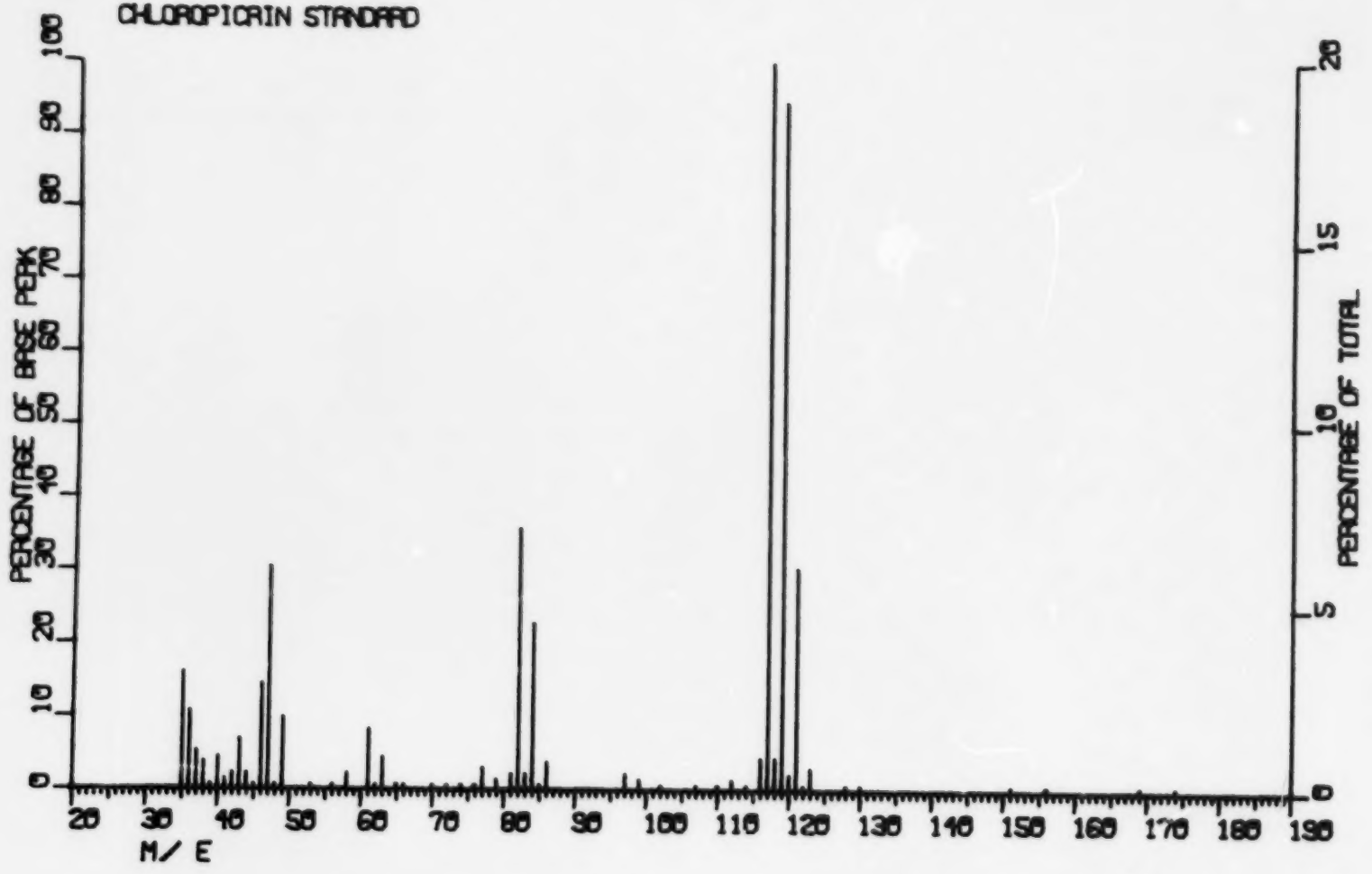

Figure 4. The mass spectrum of the compound chloropicrin, Cl_3CNO_2.

structure. Reasonableness should be based on compatibility with the accepted principles of fragmentation of organic ions in the gas phase. With magnetic deflection spectrometers, additional fractional quality points may be added if fragmentations are supported by the observation of ions from the decomposition of metastable ions.

Good spectrum matches that have a QI of 0.75-1.0 are considered reliable identifications when pure standards are not available.

Application of Analytical Quality Assurance Concepts

These AQA concepts were applied to the analyses reported in Table I. Table II summarizes the results of the tests. Bromoform, nicotine, dibromochloromethane, isophorone, trimethyl isocyanurate, benzoic acid, and phenylacetic acid were not found by EICP in the corresponding reagent blanks and each gave spectra that were good matches by inspection with spectra in the National Institutes of Health data base (7). In each spectrum the molecular ion was observed and the $M^+ + 1$ isotope accuracy or halogen isotope abundance distribution pattern was within the expected experimental error (4). In addition each compound was extracted in the expected fraction, the most volatile of the set gave short or very short retention times, and all the fragments in the mass spectra were reasonable and consistent with the assigned structure. On the basis of this evidence, these seven identifications were considered firm without recourse to authentic standards. Standards of two of the compounds were readily available, and these were used to supply additional supporting evidence.

Hexachloroethane gave a very good spectrum match by inspection and an expected short retention time; also, it was extracted in the appropriate fraction. The molecular ion was not observed, but ions were observed with halogen isotope distribution patterns that corresponded to the C_2Cl_5, C_2Cl_4, C_2Cl_3, C_2Cl_2, and CCl_3 ions. Therefore, a consistent set of fragment ions was observed and these account for all the atoms of the proposed structure. The only other reasonable possibility for this peak was pentachloroethane, and the recorded spectrum of this in the NIH data base did not exhibit a C_2HCl_5 molecular ion.

The compound di-*n*-octyl adipate was tentatively identified by the empirical matching procedure. However, no molecular ion was observed, and the complexity of the fragmentation pattern precluded a rapid determination of its consistency with the proposed structure. This is a clear example of a spectrum that contains inadequate information to permit an accurate identification without a pure reference standard. The compound was found in the acid fraction, and this also aroused suspicion about its identity since dioctyl adipate might be expected to appear in the neutral fraction.

A sample of octyl decyl adipate containing di-*n*-decyl and di-*n*-octyl-impurities was available in the laboratory. This was dosed into laboratory tap water and extracted according to the method. All the adipates were found in the acid fraction as was the adipate that was found in the Miami water sample. The retention time for dioctyl adipate was within experimental error of the retention time of the compound in the Miami water, and the observed spectrum was the same as the sample spectrum. This evidence strongly supports the identification as being that of an authentic contaminant. Its origin may be from vinyl plastic garden hose and similar materials that are in widespread use.

The compound 1,2-bis(2-chloroethoxy)ethane ($C_6H_{12}O_2Cl_2$) gave a spectrum that was in excellent agreement with the spectrum in the data base. Again, no molecular ion was observed and a reference standard was not available. However, the fragment ions at masses 63, 65 (C_2H_4Cl), 93, 95 (C_2H_4OCl), and 107, 109 (C_3H_6OCl) account for all the atoms in the compound and are consistent with the assigned structure. Two additional ions at masses 137 and 139 correspond to the loss of a CH_2-Cl group from the molecular ion. The overall evidence strongly supports the identification.

Seven other peaks were detected, but no compounds are reported because inadequate evidence was available to permit reliable identifications. Three of these appeared to be the same compound, and the available information about them is an excellent example of the application of the AQA concepts. Peaks were found at the same retention time near the detection limit of 10 ng per liter (ppt) in the neutral fractions from Miami, Cincinnati, and Philadelphia. The three mass spectra were essentially the same except for variations in the abundance of the common background ion at mass 43 (C_3H_7) and several other weak ions. The spectrum of the compound in the Cincinnati fraction is shown in Figure 3. As previously discussed, this spectrum is a good match of the spectrum of chloropicrin in Figure 4. However, since the molecular ion was not observed, interpretation of the match must be made with caution. The ions at masses 117, 119, and 121 clearly indicate the presence of a

CCl_3 group, and this is supported by the CCl_2 ions at masses 82, 84, and 86 and the CCl ions at masses 47 and 49. But there is no ion that clearly points to an NO_2 group, and the spectrum therefore fails to account for all the atoms of the proposed structure. Under these circumstances an authentic standard was required to obtain additional information. Pure chloropicrin was shown to elute much earlier than the compounds in the three neutral fractions. Therefore, although this compound contains a CCl_3 group, it remains unidentified at this time. There are small ions at masses 103 and 145 in all three spectra; these suggest the saturated oxygenated hydrocarbon ions $C_5H_{11}O_2$ and $C_8H_{17}O_2$. This compound appears similar to the 1,2-bis(2-chloroethoxy)ethane found in the Philadelphia neutral fraction: it has a longer chain and more chlorine and may be an intermediate in the formation of the ubiquitous chloroform (1). A chemical ionization mass spectrum may provide a valuable insight into the identity of this compound.

CONCLUSION

AQA is required in identifying as well as measuring the concentration of trace organics. The guidelines based on spectrum similarity and the quality of the ions found in the measured mass spectrum are a reasonable basis for evaluating the reliability of an identification.

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